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Neutral molecular cluster formation of sulfuric acid–dimethylamine observed in real time under atmospheric conditions

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For atmospheric sulfuric acid (SA) concentrations the presence of dimethylamine (DMA) at mixing ratios of several parts per trillion by volume can explain observed boundary layer new particle formation rates. However, the concentration and molecular composition of the neutral (uncharged) clusters have not been reported so far due to the lack of suitable instrumentation. Here we report on experiments from the Cosmics Leaving Outdoor Droplets chamber at the European Organization for Nuclear Research revealing the formation of neutral particles containing up to 14 SA and 16 DMA molecules, corresponding to a mobility diameter of about 2 nm, under atmospherically relevant conditions. These measurements bridge the gap between the molecular and particle perspectives of nucleation, revealing the fundamental processes involved in particle formation and growth. The neutral clusters are found to form at or close to the kinetic limit where particle formation is limited only by the collision rate of SA molecules. Even though the neutral particles are stable against evaporation from the SA dimer onward, the formation rates of particles at 1.7-nm size, which contain about 10 SA molecules, are up to 4 orders of magnitude smaller compared with those of the dimer due to coagulation and wall loss of particles before they reach 1.7 nm in diameter. This demonstrates that neither the atmospheric particle formation rate nor its dependence on SA can simply be interpreted in terms of cluster evaporation or the molecular composition of a critical nucleus.

aerosol particles | atmospheric nucleation | atmospheric chemistry | mass spectrometry

Aerosol particles are important constituents of the Earth's atmosphere. A large fraction of the particles form by nucleation of low-volatility vapors. The newly formed particles first consist only of a few molecules and have diameters between 1 and 2 nm. Under favorable conditions, where loss rates are small and growth rates are sufficiently large, the particles can reach sizes of ~50 nm where they can act as cloud condensation nuclei (CCN). Model simulations suggest that globally about half the CCN originate from new particle formation (NPF) (1). Therefore, NPF is an important process affecting the climate through the cloud albedo effect (2). Numerous studies have shown that sulfuric acid (SA; H₂SO₄) and water vapor are important compounds

participating in the formation of new particles (3, 4). However, atmospheric boundary layer NPF events cannot be explained by the binary nucleation of these two compounds alone (5); therefore, at least one additional substance besides SA and water vapor is required (6). However, the chemical identity of the compounds responsible for the high observed NPF rates remains to be fully elucidated. Recent theoretical (7, 8) and experimental (6, 9–15) studies have shown that amines efficiently stabilize SA

Significance

A significant fraction of atmospheric aerosols is formed from the condensation of low-volatility vapors. These newly formed particles can grow, become seeds for cloud particles, and influence climate. New particle formation in the planetary boundary layer generally proceeds via the neutral channel. However, unambiguous identification of neutral nucleating clusters has so far not been possible under atmospherically relevant conditions. We explored the system of sulfuric acid, water, and dimethylamine in a well-controlled laboratory experiment and measured the time-resolved concentrations of neutral clusters. Clusters containing up to 14 sulfuric acid and 16 dimethylamine molecules were observed. Our results demonstrate that a cluster containing as few as two sulfuric acid and one or two dimethylamine molecules is already stable against evaporation.

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clusters and can also form new particles together with methanesulfonic acid and water vapor (16). Other research involving amines focused on the physiochemical properties of alkylammonium sulfates (17) and on the substitution of ammonia by amines in sulfuric acid–ammonia clusters (18, 19). A recent review article summarizes the findings on the atmospheric implications of amines (20). Oxidized organic compounds can also contribute to the enhancement of NPF rates (21–25). Because neutral (uncharged) new particle formation appears to dominate in the boundary layer (26, 27), it is critically important to develop techniques to measure the composition of small neutral clusters as they grow from monomers to ultrafine particles. New particle formation is highly nonlinear with respect to the concentration of the precursor gases; therefore, it is essential for these measurements to be conducted at the (extremely low) concentrations of relevant precursor gases found in the atmosphere.

Considerable progress has been made in recent years toward the development of instruments for measurement of gaseous compounds and particles during NPF events. The number density of small particles down to ~ 1.2 nm in diameter can now be measured with the particle size magnifier (28). For charged clusters, the molecules involved can be measured with the Atmospheric Pressure interface–Time Of Flight (API-TOF) mass spectrometer (29). However, an instrument to measure the precise molecular composition of neutral clusters has been developed only very recently (30). Although atmospheric neutral clusters have previously been detected (12, 13, 31), their molecular composition was not unambiguously resolved.

Here we present results using a Chemical Ionization (CI)–API-TOF mass spectrometer that can resolve the elemental composition of neutral clusters up to $\sim 2,000$ atomic mass units (30). The largest detected clusters have a mobility diameter around 2 nm, which falls within the measurement range of recently developed condensation particle counters (28). Thus, the CI-API-TOF can measure the molecular composition of neutral clusters from the molecular up to the macroscopic size. The results shown here relate to a previous study conducted at the Cosmics Leaving Outdoor Droplets (CLOUD) chamber at the European Organization for Nuclear Research (CERN), which found that atmospheric boundary layer nucleation rates have the same range of values as particle formation rates from sulfuric acid, dimethylamine, and water (15). Almeida et al. (15) reported particle formation rates measured by condensation particle counters and showed results for charged clusters measured with an API-TOF mass spectrometer (29). One of the conclusions was, however, that ions are not essential in the formation of particles in the SA–dimethylamine (DMA) system when nucleation rates exceed a certain value. Our study reports on the very first measurements to our knowledge of neutral clusters made with a CI-API-TOF.

Results and Discussion

Ternary nucleation of SA, DMA, and water was studied using the CLOUD chamber at atmospherically relevant concentrations of SA, between $\sim 5 \times 10^5$ and 1.5×10^7 cm $^{-3}$, and with DMA [(CH $_3$) $_2$ NH] mixing ratios between 5 and 32 parts per trillion by volume (pptv). The experiments were conducted at 278 K and 38% relative humidity. Two CI-API-TOF mass spectrometers were deployed, both using nitrate charger ions (*SI Text* and *Fig. S1*).

Recent results obtained at CLOUD for the SA–DMA system showed that charged clusters containing three or more SA molecules (including the core bisulfate ion) grow by maintaining a near 1:1 ratio between the SA and DMA molecules during ion-induced nucleation (15). Here we present the first measurements, to our knowledge, of the neutral nucleating clusters. For these experiments a high-voltage clearing field is applied inside the CLOUD chamber to remove all ions and charged clusters that form due to galactic cosmic rays (5). The neutral clusters are sampled from the chamber; they only become charged upon entering the nitrate charging unit of

the CI-API-TOF instrument. The elemental composition of clusters is unambiguously identified from their exact mass-to-charge ratio due to the high mass accuracy (typically better than 10 ppm) and resolving power (maximum of 4,500 Th/Th) of the instrument. Isotopic ratios provide additional information to help resolve between atomic species.

The neutral clusters are seen to grow by stepwise addition of one SA followed by one DMA molecule (*Fig. 1 A and B*), according to the same base stabilization mechanism seen previously for charged clusters (15). The largest detected neutral cluster contains 14 SA and 16 DMA molecules. Some of the smallest clusters [tetramer and smaller, i.e., HSO $_4^-(H_2SO_4)_k$ where $k \leq 3$] are measured without DMA. However, it is likely that at least one DMA molecule is lost from the neutral clusters during the charging process because both HSO $_4^-$ and NO $_3^-$ are Lewis bases which compete with DMA to attach to a SA molecule. On the other hand, if not all HNO $_3$ evaporates from the cluster in the charging process, the evaporation of DMA can be prevented. This is indeed observed for the SA dimers [HSO $_4^-(H_2SO_4)_2$], which are detected with up to two DMA molecules (*Fig. 1B*). This is the first time to our knowledge that a stabilizing compound has been directly observed in the SA dimer. Additional evidence for the stabilizing effect of DMA on the dimers is provided by the

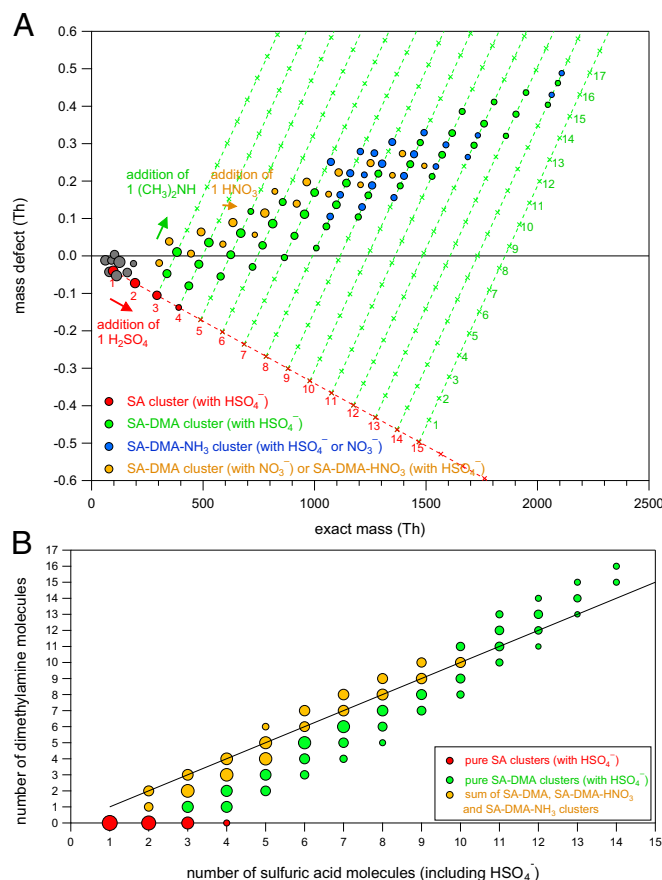


Fig. 1. Molecular weight and composition of neutral clusters during a new particle formation event with SA and DMA. (A) Mass defect plot measured with the CI-API-TOF mass spectrometer for an experiment with 10 pptv DMA and 3×10^7 cm $^{-3}$ SA. The mass defect is the difference between the exact mass and the nominal (integer) mass of the cluster. The symbol size is proportional to the logarithm of the signal intensity (count rate). Background ions and clusters (not containing SA or DMA) are indicated by gray symbols. (B) The same data with the signals grouped to show the number of SA and DMA molecules in the cluster.

magnitude of the dimer signal. For a binary system (SA and water), the dimer concentration is expected to be at least six orders of magnitude lower than seen in our measurements (32). Therefore, only stabilization by DMA can explain such high dimer concentrations (15, 33). Finally, we add that quantum chemical calculations suggest that even the neutral monomer of SA is bound to a DMA molecule (8), although this cannot yet be confirmed experimentally because DMA rapidly evaporates from the bisulfate ion.

The temporal evolution of the cluster concentrations in a single representative experiment is shown in Fig. 2. The experiment is started by turning on the UV illumination; this initiates SA production and leads to sequential appearance of progressively larger clusters. Each cluster reaches a steady-state concentration when its production and loss rates are equal. The cluster concentrations predicted by a kinetic model with unit sticking efficiency are also shown in Fig. 2. The only free parameter in the model is the monomer production rate, which was adjusted to fit the measured monomer concentration (N_1). The modeled dimer concentration (N_2) matches the experimental value within a factor of 1.5, which is within the uncertainties of the detection efficiency. The uncertainty in the measured trimer (N_3), tetramer (N_4), and pentamer (N_5) concentrations increases progressively (*SI Text* and *Fig. S2*), and the modeled concentrations of these clusters are systematically higher than the measured values.

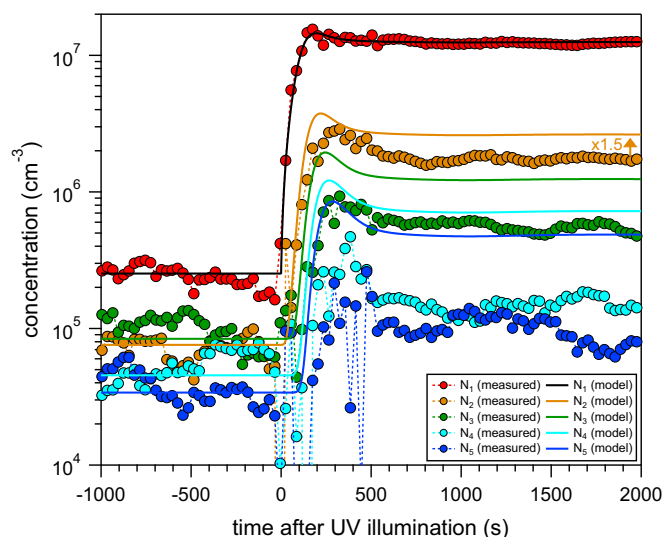


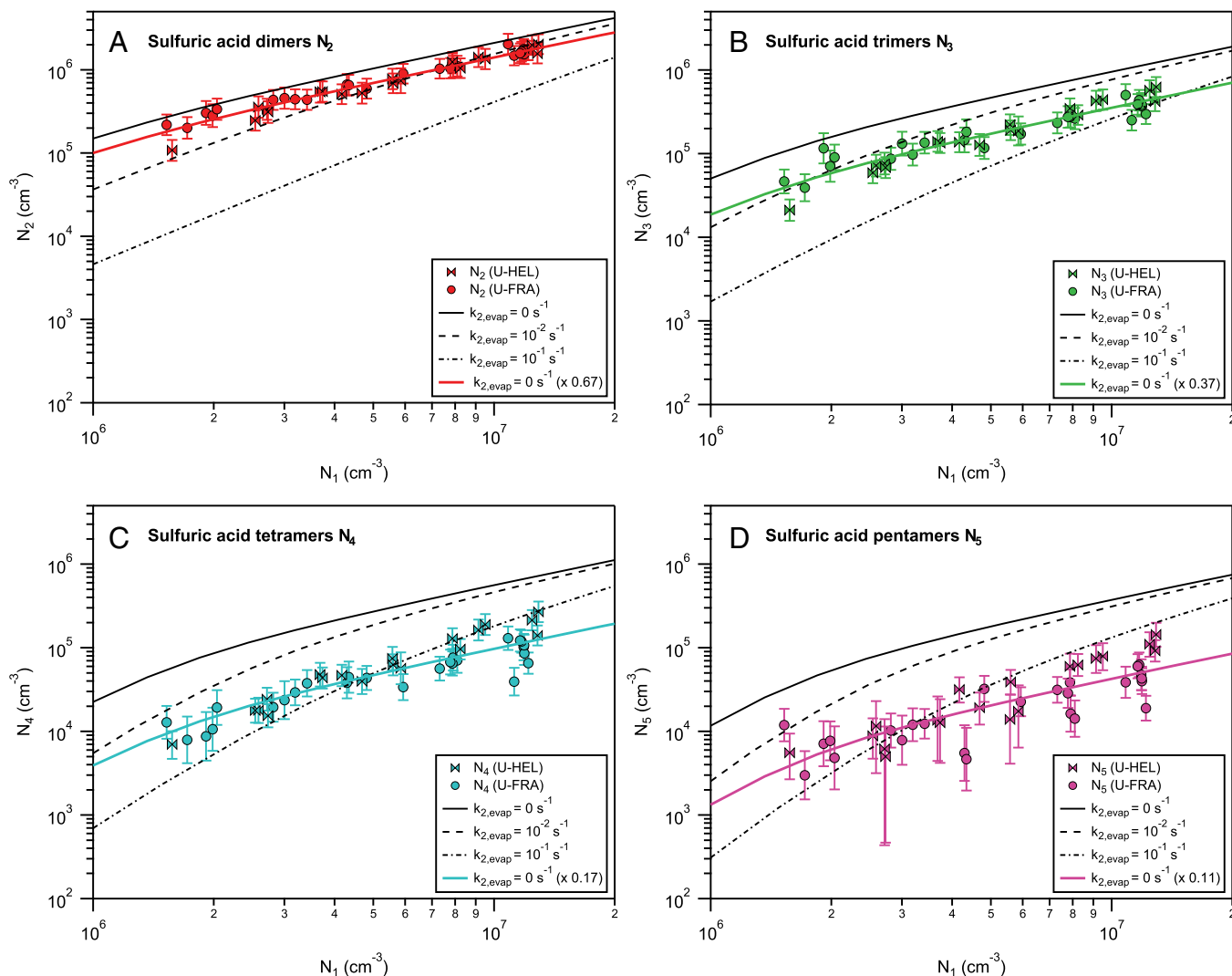
Fig. 2. Time evolution of measured and modeled neutral cluster concentrations. The concentrations were measured (circles and dashed lines) with the CI-API-TOF mass spectrometer during an experiment with 20 pptv DMA and $1.2 \times 10^7 \text{ cm}^{-3}$ SA. The notations N_1 (monomer), N_2 (dimer), N_3 (trimer), N_4 (tetramer), and N_5 (pentamer) refer to the number of sulfuric acid molecules in the cluster. To obtain the cluster concentrations (N_2 to N_5), the signals with different amounts of DMA but with a certain number of sulfur atoms are added up (*SI Text*). The experiment is started at zero time by illuminating the chamber with UV light, which initiates production of sulfuric acid monomers (N_1). The measurements are compared with calculated cluster concentrations (solid lines) from a kinetic model, which assumes that cluster evaporation rates are zero and that each collision leads to cluster growth (unit sticking efficiency). The discrepancy between the modeled and measured steady-state N_2 is indicated as a factor of ~ 1.5 . The increasing offset between measured and modeled data with increasing cluster size is consistent with a declining transmission efficiency in the CI-API-TOF. The excellent agreement on the timing of each successive cluster indicates negligible SA evaporation, confirming that the cluster growth is kinetically limited. The time resolution is 30 s. The data are smoothed by a running average except for the period where the cluster concentrations rise strongly (between 0 and 500 s).

However, when normalizing the cluster concentrations to their steady-state values, comparison between measured and modeled concentrations assuming zero evaporation shows excellent agreement (*Figs. S3* and *S4*). Therefore, these data indicate that NPF in the SA–DMA system is very likely kinetically controlled; that is, cluster evaporation rates are effectively zero. In the present work, the term “kinetically limited nucleation” refers to a situation where the cluster growth is entirely controlled by collisions with monomers and smaller clusters and not by the evaporation of monomers. Because the measured N_2 agrees with the kinetic limit calculation, this should apply also for the larger clusters because evaporation rates are expected to decrease with increasing cluster size (13, 15). The discrepancies between the modeled and measured N_k (for $k \geq 3$) in Fig. 2 can be explained by the uncertainties in deriving the concentrations from the measured cluster signals, particularly because it is presently not possible to calibrate the CI-API-TOF for cluster concentration measurements (*SI Text*). Therefore, the charging and detection efficiencies of the clusters are not well constrained and can account for the uncertainties.

The steady-state N_2 , N_3 , N_4 , and N_5 concentrations are shown as a function of the SA monomer concentration (N_1) in Fig. 3. For comparison, the modeled cluster concentrations are shown for the kinetic limit and for finite dimer evaporation rates of 0.01 and 0.1 s^{-1} . The measurements agree closely with the modeled N_2 assuming no evaporation, providing further evidence that the dimer with DMA is stable. This contrasts with earlier Chemical Ionization Mass Spectrometer (CIMS) measurements in which N_2 was about a factor of 5 lower than expected for kinetic NPF (15). Fragmentation of the $\text{HSO}_4^-(\text{H}_2\text{SO}_4)$ ions in the CIMS is the most likely explanation for this discrepancy.

For the larger clusters the measured concentrations shown in Fig. 3 are below the kinetic limit calculations (zero evaporation rate). However, it is important to note that the slopes of the experimental cluster concentrations vs. N_1 are compatible with the kinetic limit curves but incompatible with those for finite evaporation rates. Evaporation of the clusters would generally lead to a steepening of the slopes, which is not observed. Furthermore, the model curves that go through the data require progressively larger values of the dimer evaporation rate ($k_{2,\text{evap}}$), which is unphysical. In contrast, curves accounting for progressive decrease in the detection efficiency reproduce the shape of the observations with negligible SA evaporation (*SI Text*). Our measurements therefore indicate that the larger clusters also form at or near the kinetic limit. This confirms for the first time, to our knowledge, through direct measurement of neutral clusters that SA–DMA new particle formation can be a purely kinetic process. Kinetic behaviour contrasts with the observation of stable prenucleation clusters as precursors in crystallization (34). These clusters are stable up to a certain size before they reach a barrier where they become unstable before eventually crossing the nucleation barrier. Although we cannot rule out entirely that such a barrier could also exist in the SA–DMA system, it would almost certainly be beyond the pentamer. The reason is that otherwise, no monotonic decrease, but rather a sharp step, should become visible when plotting the ratio between measured and modeled cluster concentration as a function of cluster size (*SI Text* and *Fig. S2*). The data from Fig. 1*B* provide further qualitative information that even beyond the pentamer, no sharp drop in the cluster signal is visible for clusters as large as 2 nm in mobility diameter.

Chen et al. (13) concluded that nucleation of SA and base molecules (ammonia and/or amines) is not proceeding at the kinetic limit and that an evaporation rate of 0.4 s^{-1} for the trimer containing at least one base molecule can explain the atmospheric particle formation rates in Atlanta and Mexico City. This contrasts with our finding that cluster evaporation rates are negligible in the SA–DMA system. However, one needs to keep in mind that the DMA concentration is also an important



quantum chemical calculations suggest that there is only a weak dependency for SA–DMA new particle formation on temperature (15). Using the same quantum chemical methods, this has also been concluded for the effect of relative humidity (RH). Varying the RH between 0 and 100% did only lead to a small increase of about a factor of 2 in the particle formation rates even when the DMA mixing ratio was as low as 0.1 pptv [at a SA concentration of $2 \times 10^6 \text{ cm}^{-3}$ (15)]. Regarding the effect of water on the nucleation process, it is important to note that although SA and DMA molecules are not evaporating from the clusters, condensed water molecules can evaporate. However, our data indicate that this does not have a substantial effect on the SA–DMA cluster stability, and therefore, the nucleation process is termed “kinetically limited.”

Molecular cluster measurements allow direct determination of the NPF rate at a given cluster size because at steady-state concentration, the formation (nucleation) rate equals the total loss rate (to larger clusters, chamber walls, etc.). The dimer formation rate J_{dimer} versus SA monomer concentration is shown in Fig. 4. The dimer formation rates agree well with a simple analytical expression for the maximum possible NPF rate of SA particles (13) (solid line in Fig. 4). In comparison, the NPF rates at 1.7 nm are lower by 2–4 orders of magnitude (15). The difference between the NPF rates at these two sizes (J_{dimer} vs. $J_{1.7\text{nm}}$) is due to losses during growth to 1.7 nm. Both the chamber walls and the clusters/particles act as condensation sinks for the growing clusters. The losses are largest at slow growth rates, corresponding to low SA concentration (37). In the atmosphere the condensation of vapors and clusters onto preexisting particles is similar to condensation on the walls of chamber experiments. In consequence the magnitude and slopes of experimental measurements of J vs. $[\text{H}_2\text{SO}_4]$ at a chosen threshold size do not provide direct

information on cluster evaporation or on the number of molecules in the critical cluster (37, 38). This is dramatically demonstrated in Fig. 4 because the SA dimer with DMA is already a stable particle, above the size of the critical cluster. For other systems where NPF is not proceeding at the kinetic limit, different cluster sizes would need to be chosen to determine the nucleation rates. Nevertheless, similar losses and slope distortions would occur between the critical size and the chosen particle threshold size. Regarding atmospheric nucleation, it is important to note that growth rates; condensation sinks; particle sizes, at which the formation rates have been determined; and probably also the chemical systems differ between different atmospheric observations. Therefore, it cannot be concluded that atmospheric nucleation is generally a kinetic process, although there is some overlap between the formation rates for the SA–DMA system and the boundary layer particle formation rates.

Conclusions

Because atmospheric boundary layer nucleation is generally dominated by the neutral nucleation pathway, it is of utmost importance to study the formation of neutral clusters (6, 26, 27). Additionally, recent CLOUD chamber studies demonstrated that ion-induced nucleation is not substantial when the particle formation rates exceed $\sim 1 \text{ cm}^{-3} \cdot \text{s}^{-1}$ in nucleating systems involving SA as well as DMA or oxidized organics (15, 25). In this study, the formation of neutral clusters containing up to 14 SA and 16 DMA molecules was observed for the first time to our knowledge during NPF in the CLOUD chamber, including their temporal evolution.

The formation of the neutral SA–DMA clusters follows a stoichiometry of very close to 1:1 largely independent of the investigated SA and DMA concentrations. This reveals that full neutralization of sulfuric acid with respect to its acidity does not occur at the observed cluster sizes because this would require a stoichiometry of 1:2 between acid and base.

We have shown that NPF of neutral SA–DMA clusters under atmospheric conditions proceeds at or near the kinetic limit, implying negligible evaporation, which is equivalent to the notion that the critical cluster size is smaller than the dimer. We find that the NPF rate of neutral SA dimers versus $[\text{H}_2\text{SO}_4]$ in the presence of DMA proceeds at the maximum rate expected for kinetically limited NPF, with a power dependence on $[\text{H}_2\text{SO}_4]$ of 2. However, due to particle losses, the formation rate at 1.7 nm is up to 4 orders of magnitude lower than the dimer formation rate and has a power dependence near 3.7. The implication is that the translation of experimental results into mechanisms appropriate for the atmosphere will require an understanding of the kinetics of NPF, growth, and loss from the first molecular collisions (39). Most importantly, cluster loss via collisions with larger particles, and not evaporation, can dominate for even the smallest clusters (40). We have developed a detailed understanding for the neutral SA–DMA system here, and similar progress now seems achievable for various other atmospherically relevant systems.

Methods

The CLOUD chamber at CERN allows nucleation experiments to be conducted under exceptionally clean and well-defined conditions (5, 15). The 26.1-m³ electropolished stainless steel chamber is filled with artificial air by mixing nitrogen and oxygen from cryogenic liquids at a ratio of 79:21. Additionally, H₂O, O₃, and SO₂ can be added; together with UV light, which is fed into the chamber by means of a sophisticated fiber-optic system, this allows the photolytic generation of H₂SO₄. Dimethylamine from a gas bottle diluted with nitrogen was fed into the chamber during the experiments studying the NPF of SA and DMA. Two magnetically driven mixing fans ensured the rapid distribution of DMA and the other trace gases. Contact between plastic materials and the gases flowing into the chamber is avoided to minimize the abundance of spurious compounds. The chamber temperature is precisely controlled ($\pm 0.01 \text{ K}$) and can be adjusted between 208 and 373 K. During all experiments discussed here, the temperature was 278 K, and the relative humidity was 38%. One of the main purposes of the CLOUD facility is to study

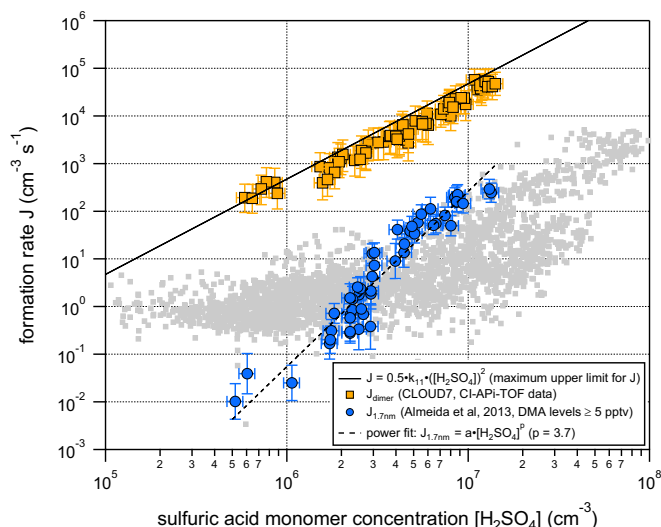


Fig. 4. Experimental, atmospheric, and theoretical particle formation rates against sulfuric acid monomer concentration (i.e., $[\text{H}_2\text{SO}_4]$ or N_1). Atmospheric boundary layer particle formation rates are shown by small gray squares (4, 6, 36). Formation rates for SA–DMA particles at a mobility diameter of 1.7 nm ($J_{1.7\text{nm}}$) previously measured by CLOUD at 5–140 pptv dimethylamine (DMA) are shown by the blue circles (15). These formation rates were derived using the standard method for calculating J at a small size (39). A power law fit ($J = a \cdot [\text{H}_2\text{SO}_4]^p$) yields a slope of $p = 3.7$ for $J_{1.7\text{nm}}$ (dashed line). Neutral dimer formation rates from the present work are indicated by the orange squares (J_{dimer}). The maximum possible particle formation rate from kinetic sulfuric acid new particle formation is indicated by the solid curve ($J = 0.5 \cdot k_{11} \cdot [\text{H}_2\text{SO}_4]^2$), where k_{11} is the collision rate between two sulfuric acid molecules (13). The difference between the kinetic dimer formation rate and the observed $J_{1.7\text{nm}}$ is almost entirely due to loss of the small clusters.

the influence of ions on nucleation and particle growth. Ions can be created by galactic cosmic rays and a pion beam from the CERN proton synchrotron. However, for the experiments shown here, an ion-free environment was required. Therefore, ± 30 kV were applied to two opposing high-voltage field cage electrodes installed inside the CLOUD chamber. The strong electric field eliminates all ions within about 1 s and allows the neutral nucleation pathway to be studied. The data shown in this study were obtained by using the CI-API-TOF (Tofwerk AG and Aerodyne Research) technique (30) (*SI Text*). The CI-API-TOFs include a CI charging unit where nitrate ions $[\text{NO}_3^-(\text{HNO}_3)_{0-2}]$ are mixed with the gas sampled from the CLOUD chamber. The primary ions rapidly react with free H_2SO_4 molecules and SA-DMA clusters at ambient pressure and produce distinct product ions. Using the API, the ions can be transferred from the reaction zone into a TOF mass spectrometer. Owing to the high mass resolving power and mass accuracy the elemental composition of the measured ions can be determined. The data were analyzed with the MATLAB-based software package tofTools (29). Dimethylamine mixing ratios were determined from measurements with an ion chromatograph (15, 41).

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